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(54) **LIANT DE REACTION POLYURETHANE A UN COMPOSANT**
(54) **SINGLE-COMPONENT POLYURETHANE REACTION**
ADHESIVE

(57) L'invention concerne un liant de réaction polyuréthane à un composant à base d'au moins un polyisocyanate, d'au moins un composé oligomère réagissant par rapport à des groupes isocyanate et d'au moins un catalyseur. Ce liant de réaction se caractérise en ce qu'il contient au moins une amine tertiaire comportant au moins un groupe fonctionnel, à incorporer comme catalyseur dans la chaîne polymère, ce qui permet de parvenir à un temps de durcissement, ainsi qu'à un temps de stockage acceptables. Les catalyseurs connus présentent le double inconvénient d'avoir des temps de durcissement trop longs pour des applications pratiques ou une stabilité au stockage insuffisante.

(57) Disclosed is a single-component polyurethane reaction adhesive based on at least one polyisocyanate, at least one oligomer compound which is reactive to isocyanate groups, and at least one catalyst. The proposed adhesive is characterised in that it contains at least one tertiary amine with at least one functional group for incorporation as a catalyst in the polymer chain, which brings the setting time down, and the shelf life up, to acceptable levels. With known catalysts, either the setting time is too long for practical applications or the shelf life is too short.

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<p>(54) Title: SINGLE-COMPONENT POLYURETHANE REACTION ADHESIVE</p> <p>(54) Bezeichnung: EINKOMPONENTEN-POLYURETHAN-REAKTIONSKLEBSTOFF</p> <p>(57) Abstract</p> <p>Disclosed is a single-component polyurethane reaction adhesive based on at least one polyisocyanate, at least one oligomer compound which is reactive to isocyanate groups, and at least one catalyst. The proposed adhesive is characterised in that it contains at least one tertiary amine with at least one functional group for incorporation as a catalyst in the polymer chain, which brings the setting time down, and the shelf life up, to acceptable levels. With known catalysts, either the setting time is too long for practical applications or the shelf life is too short.</p> <p>(57) Zusammenfassung</p> <p>Es wird ein Einkomponenten-Polyurethan-Reaktionsklebstoff auf der Basis mindestens eines Polyisocyanates, mindestens einer gegenüber Isocyanatgruppen reaktiven Oligomerverbindung und mindestens eines Katalysators beschrieben, der dadurch gekennzeichnet ist, daß er mindestens ein tertiäres Amin mit mindestens einer funktionellen Gruppe zum Einbau in die Polymerkette als Katalysator enthält. Damit wird sowohl die Aushärtungszeit als auch die Lagerzeit akzeptabel. Bei Verwendung bekannter Katalysatoren ist entweder die Aushärtungszeit für praktische Anwendungen zu lang oder die Lagerstabilität zu gering.</p>		

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A One-component Reactive Polyurethane Adhesive

This invention relates to an NCO-terminated one-component reactive polyurethane adhesive (1-C reactive PUR adhesive) based on at least one polyisocyanate, at least one NCO-reactive oligomer and at least one catalyst and to its production and use.

1-C reactive PUR adhesives are known (see, for example, Habenicht, Gerd "Kleben: Grundlagen, Technologie, Anwendungen", 2nd Edition, 1990, pages 65 and 66). They normally contain aromatic polyisocyanates and polyols or NCO prepolymers produced therefrom, catalysts and other additives. In the presence of atmospheric moisture, they set in 10 to 60 minutes. The catalysts are usually tin compounds and/or tertiary amines used in concentrations of up to 1% by weight. Higher catalyst concentrations generally lead to unstable adhesives because they also accelerate secondary reactions by which viscosity is excessively increased within a few months. In general, aromatic 1-C reactive PUR adhesives are brownish in color or gradually turn brown where they are based on aromatic isocyanates. In addition, they have to appropriately labelled on account of the aromatic polyisocyanates, their vapor pressure and their toxicology.

1-C reactive PUR adhesives of aliphatic diisocyanates are also known. Trimerization products of aliphatic diisocyanates would be particularly advantageous because they only contain small amounts of volatile isocyanates and, accordingly, would be toxicologically safe and would not have to be labelled. Unfortunately, aliphatic isocyanates have the disadvantage that they react far more slowly than aromatic isocyanates. Because of this, they are unsuitable for many practical applications.

Accordingly, the problem addressed by the present invention was to

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provide a 1-C reactive adhesive which would react more quickly than the known systems, but which would nevertheless be stable in storage and would show hardly any deterioration, but rather an improvement, in their other properties, for example toxicology.

The solution provided by the invention is defined in the claims and consists essentially in the use as catalysts of tertiary amines which combine firmly with the polymer chains. The catalyst concentration can thus be increased several times without any danger of the catalyst migrating, for example, like a plasticizer or giving rise to toxicological disadvantages.

The 1-C reactive PUR adhesive according to the invention is thus characterized in that it contains at least one tertiary amine containing at least one functional group for incorporation in the polymer chain as catalyst. The number of functional groups in the tertiary amine is preferably two although three functional groups or just one functional group may also be present per tertiary amine.

The number of reactive tertiary amines is at least - and preferably - 1. However, two different tertiary amines differing, for example, in their functionality may also be effectively used. Theoretically, there is no upper limit to the number of reactive tertiary amines although, in practice, it should not be any greater than 5. The tertiary amine may be completely or partly replaced by a quaternary ammonium compound.

The reactive tertiary amines advantageously contain the following functional groups: -OH, -SH, -COOH, -NCO, -NH₂ and -NHR, where R is an alkyl group containing 1 to 25 carbon atoms. Amines containing hydroxyl groups are preferably used. Specific compounds are N,N-dimethyl ethanolamine, N,N-dimethyl diaminoethane, N-methyl diethanolamine, N,N-dimethyl-2-(2-dimethylaminoethoxy)-ethanol, N,N,N-trimethyl-N-hydroxyethyldiaminoethane bisaminoethyl ether, N,N-bis-(3-dimethylaminopropyl)-N-isopropanolamine, tetramethyl iminobispropylamine and N-(3-dimethylaminopropyl)-N,N-

diisopropanolamine.

The reactive tertiary amine should advantageously be used in a quantity of 1 to 30 g and preferably in a quantity of 2 to 10 g per 100 g of prepolymer. Outside these ranges, disadvantages arise, i.e. there is either a distinct reduction in reactivity or the adhesive becomes brittle.

By virtue of the high catalyst concentration, even aliphatic isocyanate groups react sufficiently quickly at room temperature and, in spite of this, are surprisingly stable in storage.

1 to 5 and preferably 1 or 2 polyfunctional aromatic and aliphatic isocyanates and/or oligomerized products containing NCO groups obtained therefrom may be used to produce the one-component reactive PUR adhesive according to the invention. By "polyfunctional" is meant a functionality of the isocyanate component of greater than 1.0. The isocyanate component may even be a mixture of isocyanates.

Suitable polyfunctional isocyanates preferably contain on average 2 to at most 5 and preferably up to 4 NCO groups. Examples of suitable isocyanates are phenyl isocyanate, 1,5-naphthylene diisocyanate, 4,4'-diphenyl methane diisocyanate (MDI), hydrogenated MDI (H_{12} MDI), xylylene diisocyanate (XDI), tetramethyl xylylene diisocyanate (TMXDI), 4,4'-diphenyl dimethyl methane diisocyanate, di- and tetraalkyl diphenyl methane diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, the isomers of toluene diisocyanate (TDI), optionally in admixture, 1-methyl-2,4-diisocyanatocyclohexane, 1,6-diisocyanato-2,2,4-trimethyl hexane, 1,6-diisocyanato-2,4,4-trimethyl hexane, 1-isocyanato-methyl-3-isocyanato-1,5,5-trimethyl cyclohexane (IPDI), chlorinated and brominated diisocyanates, phosphorus-containing diisocyanates, 4,4'-diisocyanatophenyl perfluoroethane, tetramethoxybutane-1,4-diisocyanate, butane-1,4-diisocyanate, hexane-1,6-diisocyanate (HDI), dicyclohexyl methane diisocyanate, cyclohexane-1,4-diisocyanate, ethylene diisocyanate,

phthalic acid-bis-isocyanatoethyl ester, polyisocyanates containing reactive halogen atoms, such as 1-chloromethylphenyl-2,4-diisocyanate, 1-bromomethylphenyl-2,6-diisocyanate, 3,3-bis-chloromethylether-4,4'-diphenyldiisocyanate. Sulfur-containing polyisocyanates are obtained, for example, by reacting 2 moles of hexamethylene diisocyanate with 1 mole of thiodiglycol or dihydroxydihexyl sulfide. Other important diisocyanates are trimethyl hexamethylene diisocyanate, 1,4-diisocyanatobutane, 1,12-diisocyanatododecane and dimer fatty acid diisocyanate. Also of interest are partly masked polyisocyanates from which self-crosslinking polyurethanes can be formed, for example dimeric toluene diisocyanate, or polyisocyanates completely or partly reacted with, for example, phenols, tertiary butanol, phthalimide, caprolactam.

In one particular embodiment, the isocyanate component partly contains dimer fatty acid isocyanate. Dimer fatty acid is a mixture of predominantly C_{36} dicarboxylic acids which is obtained by thermal or catalytic dimerization of unsaturated C_{18} monocarboxylic acids, such as oleic acid, tall oil fatty acid or linoleic acid. Dimer fatty acids have long been known to the expert and are commercially available. The dimer fatty acid can be reacted to form dimer fatty acid isocyanates. Technical dimer fatty acid diisocyanate contains on average at least two and less than three isocyanate groups per molecule of dimer fatty acid.

Diisocyanates trimerized to isocyanurates, for example the isocyanurate of HDI and IPDI, are particularly suitable for the production of low-diisocyanate 1-C reactive PUR adhesives. It is known that the trimerization reaction takes place in the presence of suitable trimerization catalysts (see, for example, *Kunststoff-Handbuch*, Vol. 7, *Polyurethane*, page 108). Mixture of cyclotrimers of aliphatic and cycloaliphatic diisocyanates, more particularly mixed trimers thereof, are particularly advantageous.

The higher homologs of MDI containing three and more isocyanate

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groups per molecule (= polymer MDI) which may be obtained, for example, by removal of the difunctional isocyanate from the technical MDI (= crude MDI) by distillation are also suitable for the same purpose. The same applies to the so-called tri-MDI, the trifunctional homolog of MDI.

The principal component of the polyisocyanates in quantitative terms are preferably higher homologs of MDI (polymer MDI) or aliphatic polyisocyanates, more particularly trimerized diisocyanates and, above all, trimerized HDI.

It can be of advantage to use oligomerized NCO-terminated adducts of the above-mentioned isocyanates and polyols, polyamines or aminoalcohols, more particularly adducts of aliphatic isocyanates.

Preferably 1 to 5 and more preferably 1 to 3 of the organic polyhydroxyl compounds known per se in PUR chemistry for the production of high molecular weight compounds may be used as the polyols. Particularly suitable polyols are the polyhydroxypolyethers known per se which have a molecular weight of 60 to 10,000 and preferably 70 to 6,000 and which contain 2 to 10 hydroxyl groups per molecule. Polyhydroxypolyethers such as these are obtained in known manner by alkoxylation of suitable starter molecules, for example water, propylene glycol, glycerol, trimethylolpropane, sorbitol, cane sugar, aminoalcohols, such as ethanolamine or diethanolamine, or aliphatic amines, such as n-hexylamine, or 1,6-diaminohexane, or mixtures of such starter molecules. Suitable alkoxyating agents are, in particular, propylene oxide and optionally ethylene oxide.

The usual polyester polyols with molecular weights of 400 to 10,000 may also be used for the production of foams providing they contain 2 to 6 hydroxyl groups. Suitable polyester polyols are the reaction products known per se of excess quantities of polyhydric alcohols of the type already mentioned by way of example as starter molecules with polybasic acids such as, for example, succinic acid, adipic acid, phthalic acid, tetrahydrophthalic

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acid or mixtures of such acids.

Polycarbonate polyols may also be used.

It is also possible in accordance with the invention to use a) partial esters of saturated and unsaturated fatty acids with polyhydroxy compounds and ethoxylated or propoxylated derivatives thereof, b) saturated and unsaturated fatty alcohols, c) starch, sugar and cellulose and derivatives thereof, d) ring-opening products of epoxidized triglycerides or fatty acid esters with alcohols, carboxylic acids, amines and water and corresponding alkoxyated derivatives and e) castor oil or castor oil derivatives.

Instead of alcohols, polyfunctional primary or secondary amines may also be used as chain constituents. The same also applies to aminocarboxylic acids and low molecular weight protein compounds. Specific examples are polyoxyethylene, polyoxypropylene and polyoxybutylene diamine (both the homopolymers and the copolymers based on these monomers) with molecular weights of up to 5,000 (Jeffamine) and glycine, alanine, valine, leucine, cysteine, cystine, aspartic acid, glutamic acid, tyrosine, tryptophane, ϵ -aminocaproic acid, 11-aminoundecanoic acid, 4-aminobutyric acid, mono- and diaminonaphthoic acid. The percentage content of these substances should be less than 20 mole-% and is preferably 10 mole-%, based on the polyols.

Polyether and/or polyester polyols are preferably used as the polyols.

In order to limit functionality, up to 30% of the NCO groups may react with monofunctional substances, more particularly with monoalcohols, monoamines and monocarboxylic acids.

Where the polyfunctional isocyanates are reacted with polyhydroxyfatty acids, the equivalent ratio of isocyanate groups (NCO) to groups containing active hydrogen (ACH) should be 2:1 to 0.5:1 and is preferably 1.5:1 to 0.6:1.

If, in addition to the described reactions with compounds containing active hydrogen, it is also desired to trimerize excess isocyanate groups, the ratio

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of NCO to active hydrogen may even be as high as 5:1.

The isocyanate content of the adhesive according to the invention is from 0.5 to 20 g NCO/100 g adhesive and, more particularly, from 1 to 15 g NCO/100 g.

Besides the catalysts according to the invention, the usual catalysts may also be used, including in particular the following tertiary amines: diazabicyclooctane (Dabco), triethylamine, dimethylbenzylamine (Desmorapid DB, BAYER AG), bis-dimethylaminoethyl ether (Catalyst A I, UCC), tetramethyl guanidine, bis-dimethylaminomethyl phenol, 2,2'-dimorpholinodiethyl ether, 2-(2-dimethylaminoethoxy)-ethanol, 2-dimethylaminoethyl-3-dimethylaminopropyl ether, bis-(2-dimethylaminoethyl)-ether, N,N-dimethyl piperazine, N-(2-hydroxyethoxyethyl)-2-azanorbornane, Tacat DP-914 (Texaco Chemical), Jeffcat™, N,N,N,N-tetramethylbutane-1,3-diamine, N,N,N,N-tetramethylpropane-1,3-diamine, N,N,N,N-tetramethylhexyl-1,6-diamine.

The catalysts may also be present in oligomerized or polymerized form, for example as N-methylated polyethyleneimine.

Other suitable catalysts are 1-methyl imidazole, 2-methyl-1-vinyl imidazole, 1-allyl imidazole, 1-phenyl imidazole, 1,2,4,5-tetramethyl imidazole, 1-(3-aminopropyl)-imidazole, pyrimidazole, 4-dimethyl aminopyridine, 4-pyrrolidinopyridine, 4-morpholinopyridine, 4-methylpyridine and N-dodecyl-2-methyl imidazole.

Besides the tertiary amines, other catalysts may be added, including above all organometallic compounds, such as tin(II) salts of carboxylic acids, strong bases, such as alkali metal hydroxides, alcoholates and phenolates, for example di-n-octyl tin mercaptide, dibutyl tin maleate, diacetate, dilaurate, dichloride, bisdodecyl mercaptide, tin(II) acetate, ethyl hexoate and diethyl hexoate or lead phenyl ethyl dithiocarbamate. Suitable trimerization catalysts are DABCO, TMR-2, etc. (Air Products) which are quaternary ammonium salts dissolved in ethyl glycol.

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In addition, the reactive adhesive according to the invention may also contain typical additives such as, for example, fibrous fillers, pigments, defoamers, coupling agents, plasticizers, antiagers and CO₂-absorbing or adsorbing additives, for example molecular sieves and silica gel. However, substances which react chemically with CO₂, for example CaO, may also be added.

The reactive adhesive according to the invention has a medium to paste-like viscosity (ca. 200 to 100,000 mPas) and, more particularly, a medium to thick viscosity (ca. 200 to 20,000 mPas) at its application temperature. The viscosity of the adhesive changes little in storage, i.e. the adhesive remains usable. Specifically, the viscosity of the adhesive changes by at most -50 to +100% and, more particularly, by only -30 to +50%, based on the initial viscosity, after storage for 4 months at 40°C in the absence of moisture. The viscosity of the adhesive is measured with a Brookfield viscosimeter.

The reactive adhesive according to the invention contains NCO groups in such quantities that significant hardening subsequently occurs. The NCO content should advantageously be in the range from 0.5 to 20 g NCO per 100 g adhesive, as determined in accordance with DIN 53185 and DIN 16945 or ASTM-D 1638.

The reactive adhesive according to the invention may be produced in the usual way. Its production is preferably controlled in such a way that low-monomer end products are obtained.

The reactive adhesive according to the invention has the following advantages:

1. It cures very quickly when applied in a thin layer; on wood for example, it cures in about 3 to 15 minutes at room temperature (20°C), even where aliphatic polyisocyanates are used.
2. Despite its rapid curing, the reactive adhesive is sufficiently stable in

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storage, i.e. its viscosity changes by only -50 to +100% and preferably by only -30 to +50% after storage for 4 months at 40°C in the absence of moisture.

3. The physical properties of the reactive adhesive are not adversely affected by the addition of the reactive catalyst. The same applies to its flow properties.
4. Glass-clear reactive PUR adhesives can be produced.
5. The adhesive is universally usable because it adheres to many substrates.
6. The adhesive is non-toxic and is therefore particularly suitable as a household adhesive.

By virtue of the advantages mentioned above, the 1-C reactive PUR adhesive according to the invention may be used as an adhesive, as a coating composition or as a sealant, more particularly as a multipurpose adhesive (household adhesive), assembly adhesive, structural adhesive, paper and packaging adhesive, film lamination adhesive or hotmelt adhesive.

The invention is illustrated by the following Examples.

I. Starting materials

1. Polyisocyanate

- a) Tris-(6-isocyanatohexyl)-isocyanurate
- b) Desmodur DA: a hydrophilic aliphatic polyisocyanate.

2. Polyol

- a) PEG 400: polyethylene glycol, OH value 281.0
- b) PPG 400: polypropylene glycol, OH value 263.0
- c) PolyTHF 650: polytetrahydrofuran, OH value 168
- d) Desmophen C 200: polycarbonate polyol.

3. Catalyst

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- a) DBTL: dibutyl tin laurate
- b) BHPA: N,N-bis-(2-hydroxypropyl)-N,N-dimethyl-1,3-propanediamine

II. Production of 1-C reactive PU adhesives:

Adhesives are produced as follows from the above-mentioned starting materials used in the quantities shown in the Table (in g/100 g prepolymer): all the components are stirred for 2 to 3 hours at 70 to 90°C in the absence of moisture until there is no further change in the NCO content.

The NCO content was determined in accordance with DIN 53185 and DIN 16945 or ASTM-D 1638.

III. Testing of the adhesives

After conditioning at 23°C, samples are tested as follows:

Tensile shear strength (TSS) was determined by bonding beechwood test specimens stored at 23°C/50% relative air humidity with a single overlap and measuring the tensile shear strengths after 3 days using a tensile shear tester (50 mm/min.).

Setting time was determined by preparing test specimens in the same way as for the tensile shear test and measuring the TSS after different times. When the TSS measures about 1 MPa, the time which has elapsed up to that point corresponds to the setting time.

Stability in storage was determined by storing samples of the adhesives in closed vessels at 40°C and measuring the viscosity at 23°C after certain time intervals using a Brookfield viscosimeter.

The results are set out in the Table and show that 1-C reactive PUR adhesives based on aliphatic polyisocyanates which have acceptable cure times and storage lives are obtained with the catalysts according to the invention. Where known catalysts are used, either the cure time or the storage life is acceptable, but not both.

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Table

	Examples									
	1	2	3	4	5	6	7	8	9	10
Composition										
1. Polyisocyanate										
a) TIHC	75.0	80.5	79.5	83.8	87.2	83.1	78.5	62.7	79.8	-
b) Desmodur DA	-	-	-	-	-	-	-	-	-	85.4
2. Polyol										
a) PEG 400	11.4	19.5	18.5	11.2	2.8	-	-	-	12.2	-
b) PPG 400	5.6	-	-	-	-	11.9	-	-	-	10.3
c) Poly THF 650	-	-	-	-	-	-	16.5	-	-	-
d) Desmophen C200	-	-	-	-	-	-	-	32.3	-	-
3. Catalyst										
a) DBTL	-	0.03	2.0	-	-	-	-	-	-	-
b) BHPA	-	-	-	5.0	10.0	5.0	5.0	5.0	3.0	4.3

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Table

	Examples									
	1	2	3	4	5	6	7	8	9	10
4. Additives										
a) Aerosil 200	8.0	-	-	-	-	-	-	-	5.0	-
b) Carbon black	-	-	-	-	-	-	-	-	-	-
Properties										
1. Setting time [mins.]										
Wood/wood	1700	780	20	10	5	12	-	-	10	-
2. Tensile shear strength										
in [N/mm ²]										
Wood/wood	7.3	5.7	-	5.2	4.9	4.8	-	-	8.1	-
Wood/PVC	5.2	-	-	-	-	-	-	-	4.9	-
Wood/Alu	3.5	-	-	-	-	-	-	-	3.9	-
PMMA/PMMA	4.2	-	-	-	-	-	-	-	4.1	-
3. Storage stability	Good*	Good*	Poor**	Good*	Good*	Good*	Good*	Good*	Good*	Good*

* = Viscosity had increased by less than 30% after 4 months at 40°C

** = Polymerized

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CLAIMS

1. A one-component reactive polyurethane adhesive based on at least one polyisocyanate, at least one oligomer compound inert to isocyanate groups and at least one catalyst, characterized in that it contains at least one tertiary amine containing at least one functional group for incorporation in the polymer chain as catalyst.
2. A reactive adhesive as claimed in claim 1, characterized by the following functional groups of the tertiary amine: -OH, -SH, -COOH, -NCO, -NH₂, -NHR, where R is an alkyl group containing 1 to 25 carbon atoms.
3. A reactive adhesive as claimed in claim 1 or 2, characterized by 1 to 30 and more particularly 2 to 10 g reactive tertiary amine per 100 g prepolymer.
4. A reactive adhesive as claimed in claim 1, 2 or 3, characterized by higher homologs of MDI (polymer-MDI) or aliphatic polyisocyanates, more particularly trimerized diisocyanates and above all trimerized HDI, as the main quantitative component of the polyisocyanates.
5. A reactive adhesive as claimed in at least one of claims 1 to 4, characterized by polyether and/or polyester polyols as the polyols.
6. A reactive adhesive as claimed in at least one of claims 1 to 5, characterized by a medium to paste-like viscosity and, more particularly, a medium to thick viscosity at the application temperature.
7. A reactive adhesive as claimed in at least one of claims 1 to 6, characterized by a change in viscosity of -50 to +100% and, more particularly, -30 to +50%, based on the starting viscosity, when the adhesive is stored for 4 months at 40°C in the absence of moisture.
8. A reactive adhesive as claimed in at least one of claims 1 to 7, characterized by an NCO content of 0.5 to 20 g NCO per 100 g adhesive.
9. A process for the production of the adhesive claimed in at least one of claims 1 to 8, characterized in that the reaction is controlled in such a way that

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low-monomer end products are obtained.

10. The use of the adhesive claimed in at least one of claims 1 to 8 as an adhesive, coating composition or sealant, more particularly as a multipurpose adhesive (household adhesive), assembly adhesive, structural adhesive, paper and packaging adhesive, film lamination adhesive or hotmelt adhesive.

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